

## Accurate Calculation of Redox Potentials Using Density Functional Methods

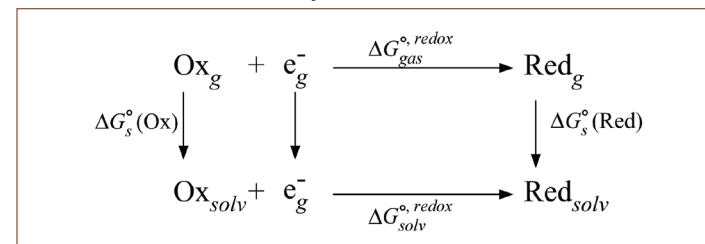
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Density functional theory (DFT) has provided insight into the mechanisms of several important catalytic cycles in environmental, bioinorganic, and industrial chemistry. Many chemical reactions utilizing transition metal complexes describe the loss and gain of electrons through the formation or breaking of chemical bonds. Combined with electrochemical and spectroscopic evidence of the pertinent intermediates, theoretical chemists have been able to deduce favorable thermodynamic and kinetic pathways to these cycles. The abilities of DFT have also been pushed in hopes of facilitating in the rational design of catalysts with specific properties. One such property that has garnered much attention over the past several years has been the ability of DFT to accurately predict redox potentials of transition metal complexes. The ability to predict redox potentials a priori is highly desirable, and one can imagine a combinatorial-computational approach to finding a redox potential within a specific range.

There are currently several protocols that exist for the theoretical prediction of the standard redox potentials in solution [1,2]. One of the more popular methods uses the Born-Haber cycle shown in Scheme 1 where the standard Gibbs free energy of redox half reaction,  $\Delta G_{solv}^{o, redox}$ , consists of the free energy change in the gas phase and the solvation free energies of the oxidized and reduced species. These values are then used to calculate the overall reaction of the standard Gibbs free energy energy,  $\Delta G_{solv}^{o, redox}$  /kcal · mol<sup>-1</sup> (Eq. 1);

$$\Delta G_{solv}^{o, redox} = \Delta G_g^{o, redox} + \Delta G_s^o(\text{Red}) - \Delta G_s^o(\text{Ox}) \quad (1)$$

**Scheme 1.** Born-Haber Cycle.



and the Nernst equation then determines the standard one-electron redox potentials,  $E^\circ/V$

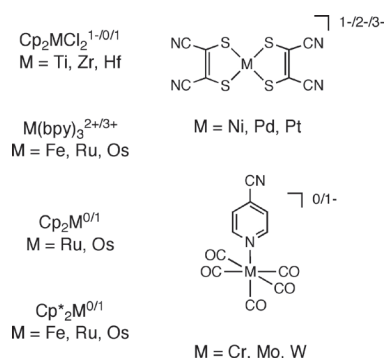
$$\Delta G_{solv}^{o, redox} = -FE_{calc}^\circ \quad (2)$$

where  $F$  is the Faraday constant, 23.06 kcal mol<sup>-1</sup> V<sup>-1</sup>.

Although this method has been successful for several organic systems using an implicit solvent model, modeling transition metal complexes has proven to be less reliable [3]. Previously, we showed that values of the calculated redox potential for a series of small models based on the diiron hydrogenase enzymes reproduced the trends experimentally with an average error of 0.12V using the gradient-corrected DFT, and results using the hybrid DFT functional required a systematic shift [4]. There, we realized the importance of referencing our results to the calculated absolute half-cell potential for the Ferrocene couple (i.e.,  $Fc + A \rightarrow Fc^+ + A^{\bullet-}$ ) in order to eliminate additional assumptions such as the solvent surface potential and the electron transfer process at the electrode surface necessary when referencing results to the experimental absolute potential of the standard hydrogen electrode (SHE). These results suggest that a fairly high degree of accuracy can be achieved for first-row transition elements. To resolve these issues, we set out to provide a rigorous quantum-chemical treatment of systems comprised of first-, second-, and third-row transition elements. These compounds contain varying oxidation states and charges and provide a good benchmark, considering the potentials are not necessarily reversible on the electrochemical time scale. Scheme 2 depicts the inorganic and organometallic compounds chosen for our study. A plot of our results

is illustrated in Fig. 1 for a typical generalized gradient approximation (GGA), functional (PBE, [5]), and the hybrid generalized gradient (H-GGA) Density Functional, (B3LYP, [6,7]), respectively. Firstly, the data are all consistent with one another for a given functional, regardless whether the redox occurs at the metal center or on the ligand.

**Scheme 2.** Transition metal complexes considered in this study.



The errors also appear to be systematic and are not dependent on whether the compound is a first-, second-, or third-row element. The PBE functional provides excellent agreement with experiment, and analysis of the data show that the quality of fit is 0.97. The B3LYP functional fared the worst in terms of fit and deviation with a systematic error of 0.83. In fact, B3LYP results require a consistent shift of -0.48 V for all the data

(shown as a dashed line in Fig. 1). When including a baseline shift for B3LYP, correlation is improved to 0.96. Examination of the data reveals that the only variation occurring with each calculation is the gas-phase free energy term,  $\Delta G_s^{\text{redox}}$ —the free energy of solvation,  $\Delta \Delta G_s^\circ$ , only differs by  $\sim 1$  kcal mol<sup>-1</sup> for all the functionals that were studied. The better performance of the GGA functional with respect to the H-GGA could be the result of an improved gas phase ionization potential.

The average error one can expect using PBE to calculate a redox couple is <0.23 V. The deviation is  $\sim 0.16$  V for the redox couple of neutral species, but larger for highly anionic or cationic complexes. This protocol is a powerful tool that will allow theoretical chemists to aid in the design of redox-active catalysts.

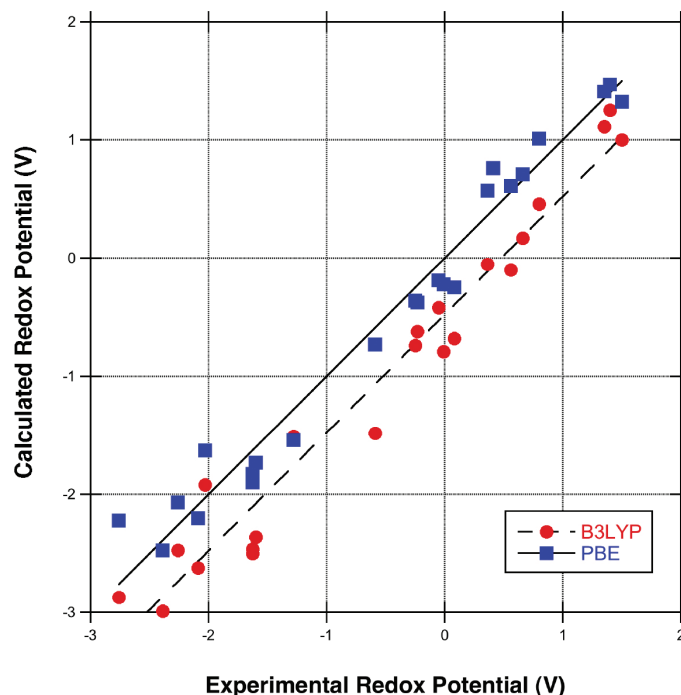


Fig. 1. Correlation diagram of experimental vs. calculated redox potential, V/Cp<sub>2</sub>Fe, for Scheme 2 complexes using PBE and B3LYP functionals. The solid line illustrates 1:1 correlation.

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